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A Diphenylcyclopropene Complex of Tungsten, $[WCl_2O(PMePh_2)_2(\eta^2\text{-}3,3\text{-diphenylcyclopropene})]$, Precursor to a Tungsten–Oxo–Olefin Metathesis Catalyst

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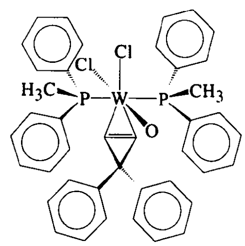
Abstract

The title compound, dichlorobis(methyldiphenylphosphine-*P*)[(1,2-η)-3,3-diphenylcyclopropene]oxotungsten, $[WCl_2O(C_{15}H_{12})(C_{13}H_{13}P)_2]$, is a mononuclear complex with an approximately octahedral environment around the metal atom. The 3,3-diphenylcyclopropene ligand is bonded to the W atom in a η^2-geometry, with effectively identical metal-to-carbon bond distances [W—C1 2.133 (7) and W—C2 2.131 (7) Å].

Comment

The development of well defined tungsten alkylidene-based metathesis catalysts has been an area of interest. In sharp contrast to the large number of arylimido-based metathesis catalysts that have been reported, there has been only one report of a tungsten–oxo–alkylidene metathesis catalyst (de la Mata & Grubbs, 1996). The title compound, (I), is a precursor to that catalyst. The active tungsten–oxo–vinyl-alkylidene is obtained from the title compound by ring opening of the cyclopropene, facilitated by the addition of lithium alkoxide salts (de la Mata & Grubbs, 1996).



(I)

Drawings of the tungsten complex are shown in Figs. 1 and 2, with a packing diagram shown in Fig. 3. The ligands are arranged around the W atom in a distorted octahedron. The phosphine ligands are *trans* with respect to one another and the P—W—P angle [154.99 (7)°] suggests there is significant steric crowding between the phosphine and olefin ligands. This steric effect is also observed in $[W(PMePh_2)_2Cl_2O(\eta^2\text{-ethylene})]$ (Su, Cooper, Geib, Rheingold & Mayer, 1986). The P—W bond distances are nearly identical; P1—W 2.590 (2) and P2—W 2.598 (2) Å. Three of the remaining coordination sites are occupied by two *cis*-chloride ligands [Cl2—W—Cl1 85.76 (7)°] and an oxo O atom [O—W—Cl1 174.3 (2) and O—W—Cl2 88.7 (2)°]. The tungsten–chloride bond *trans* to the oxo ligand (Cl1) is longer than the *cis* bond distance [Cl1—W 2.487 (2) and Cl2—W 2.471 (2) Å], consistent with the *trans* influence observed in other dichloride–tungsten–oxo complexes (Churchill & Rheingold, 1982; Chiu, Lyons, Wilkinson, Thornton-Pett & Hursthouse, 1983; Su *et al.*, 1986; Bryan, Geib, Rheingold & Mayer, 1987; Yoon, Parkin, Hughes & Leigh, 1992). The W—O distance of 1.692 (4) Å is identical to the average terminal W—O bond length reported for 22 other tungsten–oxo complexes (Orpen, Brammer, Allen, Kennard, Watson & Taylor, 1989). The last site is occupied by 3,3-diphenylcyclopropene, with the C=C bond parallel (within 0.4°) to the P···P vector. The W—C distances are identical within their e.s.d.'s [C1—W 2.133 (7) and C2—W 2.131 (7) Å] and the C=C bond is long [C1=C2 1.447 (9) Å]. Similar lengthening of the C=C bond is found in the crystal structures of other η^2-cyclopropene complexes (Johnson, Grubbs & Ziller, 1993; Li, Nguyen, Grubbs & Ziller, 1994). The two single bonds of the cyclopropene ring are slightly shortened, averaging 1.502 (6) Å. The P—C distances range from 1.800 to 1.825 Å, with an average value of 1.817 (4) Å. The C—C distances in the phenyl rings

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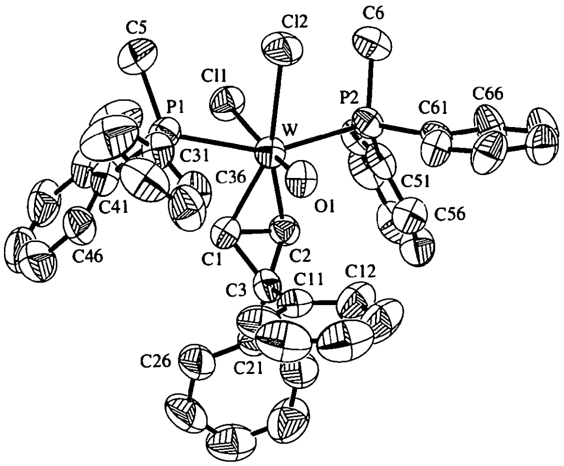

Fig. 1. Drawing of (I) showing 50% probability ellipsoids. H atoms have been omitted for clarity.

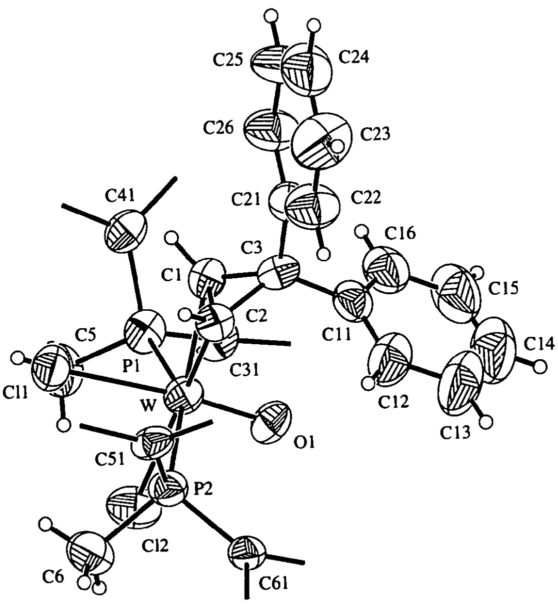

Fig. 2. Drawing of (I) with five C atoms of each phenyl ring on phosphorous omitted for clarity.

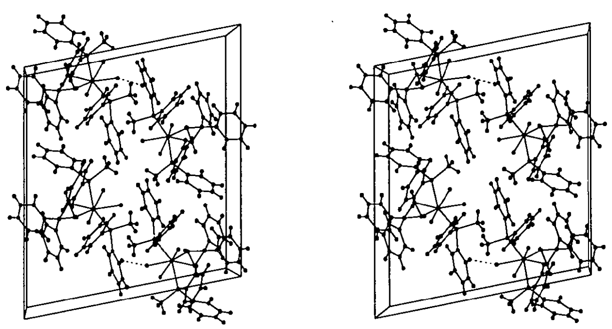

Fig. 3. Packing stereodiagram of (I) showing the unit cell and its contents.

range from 1.351 (13) to 1.406 (12) Å, with an average of 1.378 (15) Å. The reported e.s.d. of the average P—C distance is the e.s.d. of that value (the six P—C distances are statistically equal), however, the reported e.s.d. of the average C—C distance is the scatter e.s.d. derived from the values being averaged (the 36 C—C distances are not statistically equal).

Experimental

The title compound was synthesized in a dry box under a nitrogen atmosphere. A benzene solution (5 ml) containing 3,3-diphenylcyclopropene (0.486 g, 2.53 mmol) was added to a 250 ml teflon needle-valve Strauss flask containing a benzene (45 ml) slurry of $[WCl_2O(PMePh_2)_3]$ (2.00 g, 2.30 mmol). The slurry was stirred at 328 K for 12 h, then filtered through glass wool into pentane (150 ml) resulting in a pale yellow solid (90% yield, 1.78 g). This solid was washed on a medium-fritted glass filter with pentane (3 × 30 ml). Crystals suitable for X-ray diffraction studies were obtained by layering a CH_2Cl_2 solution of the pale yellow solid (200 mg, 1 ml) into 15 ml of pentane. The oxygen-sensitive crystals were fixed to a glass fibre then coated with epoxy.

Crystal data

$[WCl_2O(C_{15}H_{12})(C_{13}H_{13}P)_2]$
$M_r = 863.40$
Monoclinic
$P2_1/c$
$a = 18.494 (8)$ Å
$b = 9.857 (3)$ Å
$c = 20.886 (8)$ Å
$\beta = 100.83 (3)°$
$V = 3739 (2)$ Å^3
$Z = 4$
$D_x = 1.534$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9.5–10.3°$
$\mu = 3.35$ mm^{-1}
$T = 293 (2)$ K
Thick needle
0.4 × 0.2 × 0.2 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.42$, $T_{max} = 0.51$
11 266 measured reflections
4881 independent reflections
3671 observed reflections $[I > 2\sigma(I)]$

$R_{int} = 0.034$
$\theta_{max} = 22.5°$
$h = -19 \rightarrow 19$
$k = 0 \rightarrow 10$
$l = -22 \rightarrow 22$
3 standard reflections frequency: 60 min intensity decay: within counting statistics

Refinement

Refinement on F^2
$R(F) = 0.036$
$wR(F^2) = 0.062$
$S = 1.47$
4831 reflections
424 parameters
H atoms refined as riding
$w = 1/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 1.38$ e Å^{-3}
$\Delta\rho_{min} = -0.73$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* ($Å^2$)

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
W	0.31356 (2)	0.42740 (3)	0.61310 (2)	0.04762 (11)
Cl1	0.36047 (10)	0.2450 (2)	0.54942 (9)	0.0606 (5)
Cl2	0.43464 (11)	0.5363 (2)	0.61693 (11)	0.0761 (7)
P1	0.29081 (11)	0.5501 (2)	0.50146 (9)	0.0541 (5)
P2	0.39009 (10)	0.2891 (2)	0.70818 (9)	0.0488 (5)
O1	0.2902 (2)	0.5577 (4)	0.6579 (2)	0.0545 (13)
C1	0.2050 (4)	0.3599 (7)	0.5727 (3)	0.048 (2)
C2	0.2328 (4)	0.2865 (7)	0.6322 (3)	0.050 (2)
C3	0.1593 (4)	0.3543 (7)	0.6251 (3)	0.049 (2)
C5	0.3697 (4)	0.5525 (8)	0.4610 (4)	0.078 (3)
C6	0.4843 (4)	0.2633 (8)	0.7000 (4)	0.073 (2)
C11	0.1453 (4)	0.4759 (8)	0.6644 (4)	0.055 (2)
C12	0.1703 (5)	0.4810 (9)	0.7310 (4)	0.078 (3)
C13	0.1531 (6)	0.5937 (13)	0.7664 (5)	0.109 (4)
C14	0.1135 (7)	0.6986 (12)	0.7363 (7)	0.114 (4)
C15	0.0897 (5)	0.6976 (10)	0.6693 (7)	0.105 (4)
C16	0.1053 (4)	0.5829 (9)	0.6343 (5)	0.076 (3)
C21	0.0938 (4)	0.2596 (8)	0.6136 (4)	0.051 (2)
C22	0.0803 (5)	0.1761 (9)	0.6621 (4)	0.078 (3)
C23	0.0209 (6)	0.0878 (11)	0.6527 (5)	0.102 (3)
C24	−0.0263 (5)	0.0854 (11)	0.5937 (6)	0.095 (3)
C25	−0.0130 (5)	0.1674 (11)	0.5449 (5)	0.097 (3)
C26	0.0470 (4)	0.2553 (9)	0.5539 (4)	0.077 (3)
C31	0.2629 (4)	0.7268 (7)	0.5063 (4)	0.056 (2)
C32	0.2742 (6)	0.8191 (9)	0.4608 (5)	0.114 (4)
C33	0.2507 (6)	0.9511 (11)	0.4633 (7)	0.123 (4)
C34	0.2143 (6)	0.9922 (10)	0.5103 (6)	0.092 (3)
C35	0.2006 (5)	0.9015 (10)	0.5558 (4)	0.088 (3)
C36	0.2258 (5)	0.7676 (9)	0.5535 (4)	0.074 (3)
C41	0.2184 (5)	0.4802 (8)	0.4391 (3)	0.056 (2)
C42	0.2290 (5)	0.3543 (9)	0.4110 (4)	0.072 (3)
C43	0.1727 (6)	0.2935 (10)	0.3663 (4)	0.088 (3)
C44	0.1065 (7)	0.3614 (14)	0.3512 (4)	0.104 (4)
C45	0.0949 (6)	0.4854 (12)	0.3779 (5)	0.098 (3)
C46	0.1509 (5)	0.5419 (9)	0.4219 (4)	0.074 (3)
C51	0.3566 (4)	0.1183 (7)	0.7186 (4)	0.049 (2)
C52	0.3796 (4)	0.0089 (8)	0.6853 (4)	0.060 (2)
C53	0.3513 (5)	−0.1186 (8)	0.6916 (4)	0.069 (3)
C54	0.2987 (5)	−0.1394 (9)	0.7296 (4)	0.073 (3)
C55	0.2757 (5)	−0.0304 (8)	0.7628 (4)	0.070 (2)
C56	0.3044 (4)	0.0965 (7)	0.7570 (4)	0.058 (2)
C61	0.3990 (4)	0.3633 (7)	0.7889 (3)	0.047 (2)
C62	0.3799 (4)	0.4956 (8)	0.7974 (4)	0.060 (2)
C63	0.3930 (5)	0.5533 (9)	0.8591 (4)	0.077 (3)
C64	0.4251 (5)	0.4785 (10)	0.9120 (4)	0.076 (3)
C65	0.4446 (5)	0.3480 (10)	0.9044 (4)	0.084 (3)
C66	0.4319 (4)	0.2907 (8)	0.8431 (4)	0.070 (2)

Table 2. *Selected geometric parameters* (Å, °)

W—O1	1.692 (4)	W—P1	2.590 (2)
W—C2	2.131 (7)	W—P2	2.598 (2)
W—C1	2.133 (7)	C1—C2	1.447 (9)
W—Cl2	2.471 (2)	C1—C3	1.506 (9)
W—Cl1	2.487 (2)	C2—C3	1.497 (9)
O1—W—C2	97.5 (2)	C1—W—P2	118.4 (2)
O1—W—C1	97.9 (2)	Cl2—W—P2	80.96 (7)
O1—W—Cl2	88.7 (2)	Cl1—W—P2	80.49 (7)
C2—W—Cl2	160.0 (2)	P1—W—P2	154.99 (7)
C1—W—Cl2	158.2 (2)	C2—C1—C3	60.9 (4)
O1—W—Cl1	174.3 (2)	C1—C2—C3	61.5 (4)
C2—W—Cl1	87.5 (2)	C2—C3—C1	57.6 (4)
C1—W—Cl1	87.7 (2)	W—C1—C3	109.8 (5)
Cl2—W—Cl1	85.76 (7)	W—C2—C3	110.2 (5)
O1—W—P1	97.4 (2)	W—C1—H1	124.2 (2)
C2—W—P1	118.2 (2)	W—C2—H2	124.1 (2)
C1—W—P1	78.9 (2)	C1—C3—C11	123.1 (6)
Cl2—W—P1	79.59 (7)	C2—C3—C11	123.2 (6)
Cl1—W—P1	82.54 (7)	C1—C3—C21	116.7 (6)
O1—W—P2	97.7 (2)	C2—C3—C21	115.2 (6)
C2—W—P2	79.3 (2)	C11—C3—C21	111.4 (6)

The intensities were collected at room temperature and averaged in point group $2/m$. The variances [$\sigma^2(F_o^2)$] were derived from counting statistics plus an additional term, $(0.014I)^2$, and the variances of the merged data were obtained by propagation of error plus the addition of another term, $(0.014\langle I\rangle)^2$. The structure was solved by the Patterson method. The initial solution revealed the position of the tungsten and its seven bonded neighbors. Two successive difference Fourier maps revealed the remaining atoms. Refinement was carried out on F^2 for all reflections, except for 50 with very negative F^2. All of the H atoms were apparent in the difference maps and were included at calculated sites with their coordinates riding on the C atom to which they were attached and their displacement parameters constrained to 1.5 times the U_{eq} of the C atom. The largest peak in the final difference map is 1.38 e $Å^{-3}$ at 1.05 Å from tungsten.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CRYM* (Duchamp, 1964). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1246). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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